

# A Thermally Modified Polymer Matrix Composite Material With Structural Integrity to 371 °C

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A THERMALLY MODIFIED POLYMER MATRIX COMPOSITE MATERIAL WITH  
STRUCTURAL INTEGRITY TO 371 °C

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Abstract

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There is an ongoing search for polymer matrix composite materials that can be used for long periods of time in excess of the temperature limit for the state-of-the-art graphite/PMR-15 composite material. It is clear that both thermo-oxidative stability and structural integrity must be maintained at these elevated temperatures. In conjunction with the search for high temperature polymer matrices to accomplish the above, considerable thought has been given to protecting polymer matrix composites from oxidation with a surface coating that is impervious to air and moisture. This study was conducted to determine the potential for utilizing surface coatings to inhibit the thermal oxidation of polymer matrix composites. Answers to two questions were considered of importance before an effort should be made to initiate coating studies:

(1) Even if an effective oxygen excluding coating can be developed, will the polymer be thermally stable enough so that no thermal degradation occurs after the coating has been applied?

(2) Can the high temperature load bearing properties of a polymer matrix be improved enough to provide a stable structure at temperatures of 371 °C and above?

Isothermal, inert gas exposures of graphite/PMR-15 composites indicated that after an initial loss of weight, no significant amounts of thermal degradation products are given off during high temperature exposures in the absence of oxygen. As long as a coating remains effective, the composite material should remain stable.

It was also found that the glass transition temperature,  $T_g$ , of the

matrix resin could be increased to values in excess of 400 °C. This resulted in measured short beam shear strengths of 75.9 MPa (11 Ksi), flexural strengths of 1172 MPa (170 Ksi) and flexural moduli of 141 GPa (20.5 Msi) for the material at a test temperature of 371 °C. The treatment that was used caused a decrease in the PMR-15 resin density from 1.31 to 1.29 gm/cc. It was concluded that state-of-the-art composites, protected by oxygen-impervious coatings can be used as materials of construction with structural integrity to at least 371 °C and possibly above.

#### 1. INTRODUCTION

The state-of-the-art commercial, high temperature polymer matrix composite is used in aerospace structural components that experience service temperatures up to 316 °C. A polymer that is frequently used in the composite is PMR-15 polyimide and the reinforcement is normally continuous graphite fibers.

Current interest in aircraft engine structure applications is focused on the use of polymer matrix composites with use temperatures as high as 371 and possibly 427 °C. Depending on the nature of the structure in which it is to be used, the composite material must maintain its structural integrity for times from 100 hr to over

5000 hr in air at atmospheric and elevated pressures.

While much effort has been directed to the development of modified polyimide resins which show slight increases in thermo-oxidative stability time at temperature, there has yet to be reported a polymer matrix composite system with the level of thermo-oxidative stability and mechanical property retention at elevated temperatures that is observed for graphite/PMR-15 composites at their maximum long time use temperature (288 °C).

An alternative to trying to develop new resins, would be to test state-of-the-art polymer matrix composites under conditions that they would experience if an oxygen impervious coating were used to protect them from oxidation.

The initial concern would be the possibility for the formation and release of gaseous pyrolysis products from the interior of coated composite materials. These products could possibly disrupt the surface coating and allow eventual penetration by the oxidizing gases. Secondly, it could be possible that even if off-gassing from the composite material could be eliminated, most state-of-the-art polyimides have a glass transition temperature ( $T_g$ ) below 400 °C and therefore it would not be expected that good structural stability

should be expected at the desired use temperatures of 371 °C and above.

The work described herein was initiated primarily to determine if the use of coatings was a feasible route for improving the thermooxidative stability of matrix composite materials. Studies were directed toward measuring the thermal stability of Celion 6000/PMR-15 in an inert gaseous environment and the effects of this exposure on selected physical and mechanical properties of the material.

## 2. MATERIALS

Three monomers were used in preparing the 1500 molecular weight PMR-15 polyimide matrix. These include the monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA) and the freshly esterified 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA). Raw materials were obtained from commercial sources.

The reinforcements used in this study were the Thornel T-40R graphite fiber, the Celion 6000 graphite fiber, and Celion 6000 graphite fabric.

Esterification of BTDA to the dimethyl ester of 3,3', 4,4'-benzophenone tetracarboxylic acid (BTDE) was accomplished by refluxing the anhydride in methanol to form a 50 wt % BTDE solution. The monomer solution was prepared at room

temperature by the addition of the monomers in a 2 NE: 3.087 MDA: 2.087 BTDE stoichiometric ratio with the proper amount of methanol to make a 50 wt % solution.

## 3. LAMINATE FABRICATION AND SPECIMEN PREPARATION

The following steps were employed in prepregging and laminate fabrication:

- (1) Fiber tow winding
- (2) Tow impregnation with the monomer solution
- (3) Drying
- (4) Ply cutting and lay-up
- (5) Imidization
- (6) Compression molding

This procedure is fully described elsewhere,<sup>(1)</sup> and it yielded low void, high quality laminates. A free standing post cure in air at 316 °C for 16 hr was used to complete the curing process.

A series of three 10 ply T-40R fiber reinforced and three 12 ply Celion 6000 reinforced unidirectional composite laminates were fabricated. The laminates had nominal dimensions of 20.3 cm in the fiber direction, by 7.6 cm transverse to the fibers and approximately 0.18 cm thick. The laminates were machined into specimens having the approximate dimensions as follows:

- (1) 2.5 by 7.6 cm coupons
- (2) 1.3 by 0.51 cm flexural specimens
- (3) 2.54 by 0.51 cm shear specimens

All the laminates were examined nondestructively by ultrasonic through transmission C-scan methods and were found to be of acceptable quality.

#### 4. TEST PROCEDURE

The composite materials were aged at three different temperatures in a nitrogen atmosphere. The aging temperatures were 343, 371, and 427 °C. The materials were sealed within a 22.9 cm long by 7.6 cm diameter tube that was capped at both ends. The nitrogen entered the chamber at one end, flowed through the chamber, and exited through the other end cap. The flow was maintained at a rate of one 0.6 cm diameter bubble every second (about 55 cc/min). The incoming nitrogen was passed through a water and oxygen absorption cartridge. Periodically the materials were removed from the chamber for weighing and for the recording of dimensional measurements. The chamber was heated inside of a Blue M electric oven, Model POM 6680E-3 with a ProMaster Microprocessor Programming System. The apparatus that was used is shown schematically in Fig. 1.

Air aging of some samples was carried out concurrently with the nitrogen aging tests. The specimens were placed in the oven outside of the nitrogen cylinder. The air flow rate was 100 cc/min.

Short beam shear tests and three point flexural tests were run at room temperature and at 371 °C to

provide data for assessing the strength of the as fabricated, and aged composites. The short beam shear specimens measured 0.58 cm long by 0.508 cm wide by about 0.23 cm thick, and the flexural specimens measured 6.3 cm long by 0.508 cm wide and about 0.23 cm thick. Interlaminar shear strength tests were performed in accordance with ASTM D-2344 at a span/depth ratio of 5. The flexural tests were run in accordance with ASTM D-790 at a span/depth ratio of approximately 26. Elevated temperature tests were run in an environmental chamber. The specimens were held at the test temperature in the chamber for at least 5 min before the tests were conducted. The property values that are reported are averages of at least three tests.

A Perkin-Elmer TGS-2 Thermogravimetric System was used to measure isothermal weight loss data. Tg measurements were made by Thermal Mechanical Analysis using a DuPont 943 TMA. Both systems were connected with Omnitherm data collection and evaluation software.

Density measurements were made with a water immersion technique as described in ASTM D-792, and the fiber content of composites were measured using the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> digestion method.<sup>(2)</sup>

#### 5. RESULTS AND DISCUSSIONS

##### 5.1 Composite Weight Loss

Figure 2 shows composite weight loss data for Celion 6000/PMR-15

composites aged in air at 371 °C and in nitrogen at 342, 371, and 427 °C. The nitrogen-aged material appears to asymptotically approach stable values over a period of time at each temperature. These curves suggest that these materials, after being aged in nitrogen, can exist at the aging temperature for extended periods of time without undergoing further extensive degradation. The majority of the weight loss appears to take place within the first few hundred hours of aging. The air aged coupons were of the same size as the nitrogen aged specimens. Specimen size effects have been noted for air aging test data.<sup>(3)</sup> No size effects were observed in the data measured during nitrogen aging. It appears that very little of the composite weight loss in air can be attributed to the thermal decomposition (pyrolysis) of the polyimide matrix. Also, it appears that only the initial portion (150 hr) of the weight loss curves for the nitrogen aged materials reflect thermally activated processes since after the first 150 hr, the slopes of the three curves for the three different temperatures appear to be very close to being identical.

A closer study of the initial portion of the aging curve was carried out using the TGA. Specimens measuring 0.635 by 0.635 cm were isothermally aged for 24 hr in argon at 343, 371, and 427 °C. As can

be seen from Fig. 3, the greatest part of the weight change occurs within the first 24 hr of exposure. Since the latter parts of the curves are almost parallel, it appears that no thermal activation energy exists past the initial portion of exposure. Using the three TGA curves to measure weight loss rates at common times within the first 25 hr of aging, the activation energy for thermal degradation was calculated to be 19.2 Kcal/g mole. The activation energy for oxidation of this material was calculated to be 43 Kcal/g mole.<sup>(4)</sup> The initial weight loss rates appear to be much greater than those of the large samples. This is probably due to a faster release of decomposition products by the smaller specimens with their higher surface area to weight or volume ratio.

Figure 5 shows the plotted weight loss data measured during the aging of PMR-15 composite material in nitrogen at 371 °C for 370 hr and then after reducing the aging temperature to 343 °C, for almost 300 more hours. The weight loss increased only 0.3 percent over this time at 343 °C. These data indicate that specimen weight will stabilize at a temperature slightly lower than the maximum aging temperature. This further suggests the potential for using thermooxidatively stable coatings to produce polymer matrix composite materials suitable for use at

temperatures above the present state-of-the-art limit for advanced composites.

### 5.2 Tg Changes

Figure 4 shows TMA curves for unaged Celion 6000/PMR-15 and Celion 6000/PMR-15 composites that were aged in nitrogen at 343, 371, and 427 °C for 24 hr. The curves indicate a significant increase in the Tg due to the nitrogen aging. The increase is well over 130 °C. These results suggest that thermoplastic behavior will not influence the structural behavior of this material at elevated temperatures. Any degradation of material mechanical properties should occur from damage to the polymer structure itself.

### 5.3 Dimension and Density Changes

As with the weight loss data, the major portions of dimensional changes and density changes take place early in the thermal aging cycle. After aging in nitrogen for 25 hr at 427 °C, Celion 6000/PMR-15 composite dimensions and densities decreased to 98.6 and 99.6 percent of their as postcured values respectively. A 6 percent weight loss was observed at 25 hr of aging, so a significant amount of the total observed weight loss (8.2 percent after 230 hr) occurred during the first 25 hr of the N<sub>2</sub> exposure period. No porosity was observed in photomicrographs at a magnification of 50X. Some physical properties measurements are presented in Table 1. It appears from the results of these tests

and visual observations that the isothermal inert gas exposure of Celion 6000/PMR-15 does not significantly alter the physical nature of the material (surface, voids, cracks, etc.)

## 6. MECHANICAL PROPERTIES

Mechanical properties measurements were limited to flexural strengths and moduli and interlaminar shear strength (ILSS) tests. The test results were used to assess the effect of real time aging in an oxygen free atmosphere on the physical condition of graphite fiber polyimide composites. It was believed that any degradation that might occur would be apparent in either one of the two measured properties. The ILSS measurements were made at room temperature and at 371 °C, and the data are presented in Table 2. For the PMR-15 composite that was aged in N<sub>2</sub> at 371 °C for 335 hr and then at 427 °C for 230 hr, the retained room temperature ILSS was 51 percent. When the same material was just aged at 371 °C for 600 hr, it retained over 72 percent of its as-fabricated ILSS at room temperature. When the aging was stopped after 335 hr at 371 °C, the ILSS retention measure almost 92 percent of the unaged value.

Table 2 also presents ILSS data measured in air at 371 °C. While the strengths of the specimens have decreased in comparison to the room temperature properties, they still show a significant

amount of strength in comparison to the unpostcured and unaged samples that were tested in air at 371 °C. The great difference can be attributed to the measured increase in Tg shown in Fig. 4 for the nitrogen aged material.

A more dramatic effect of the aging process on the mechanical behavior of T-40-R/PMR-15 composite is shown in Table 3. When the material was aged in nitrogen, the flexural properties at 371 °C were increased significantly over the as fabricated material. In these tests, the composites were aged and tested at the same temperature.

#### 7. SUMMARY

While more extensive work is necessary to fully characterize this material, it appears that there are a number of potential benefits which might be gained through the use of graphite/PMR-15 composites aged in nitrogen.

The material appears to possess sufficient strength for short time structural use at 371 °C. The TMA data indicates that a significant increase in Tg occurs during the inert atmosphere aging. This explains the extraordinary mechanical properties that were measured at 371 °C.

The dimensional and density stability of this material is of special significance. Only insignificant density changes were observed in both the composite and the neat

resin after N<sub>2</sub> aging. No surface cracking or warping were observed which might be caused by residual stress buildup from changes in constituent density changes. No porosity was observed from photomicrographs of composite cross sections after aging.

If a compatible protective coating can be developed for this material, it should be suitable for long term structural use at temperatures in excess of that for uncoated graphite/polyimide composites. The limiting upper use temperature would be determined by the nitrogen aging temperature.

It appears that the possibility of using lightweight graphite fiber composites with their inherent high specific strength and specific modulus at temperatures up to 371 °C has been affirmed by the results of this study. The exploration of suitable protective coatings to prevent thermooxidative deterioration of the material would be worthwhile.

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TABLE 1. - ROOM TEMPERATURE PHYSICAL AND MECHANICAL  
PROPERTIES OF PMR-15 RESIN

	Unaged	Aged at 371 °C for 293 hr
Weight loss, mg/cm <sup>2</sup> (percent)		6.99 (7.1)
Dimen. change, percent		-2.2
Density, gm/cc	1.31	1.29
Calculated voids, percent		1.20
Flexural str., MPa (Ksi)		70.67 (10.25)
Flexural mod., GPa (Msi)	3.81 (0.55)	4.192 (0.61)

TABLE 2. - INTERLAMINAR SHEAR STRENGTH OF CELION  
6000/PMR-15 COMPOSITES AT ROOM TEMPERATURE  
AND 371 °C

	ILSS, MPa (ksi), room temp.	ILSS, MPa (ksi), 371 °C
No post cure, no aging	118.6 (17.2)	27.6 (4)
335 hr at 371 °C in N <sub>2</sub>	115.1 (16.7)	77.2 (11.2)
335 hr at 371 °C and 230 hr at 427 °C in N <sub>2</sub>	60.7 (8.8)	55.2 (8)
600 hr at 371 °C in N <sub>2</sub>	84.1 (12.2)	49 (7.1)

TABLE 3. - FLEXURAL PROPERTIES OF T-40R/PMR-15 COMPOSITES  
AT ROOM TEMPERATURE AND 371 °C

	Room temperature		371 °C	
	Strength, MPa (ksi)	Modulus, GPa (Msi)	Strength, MPa (ksi)	Modulus, GPa (Msi)
No aging	1419 (205.8)	148.2 (21.5)	482.6 (70)	84.1 (12.2)
Aged 400 hr $\eta_2$ at 371 °C	1184.6 (171.8)	148.2 (21.5)	1165.3 (169)	144.8 (21)

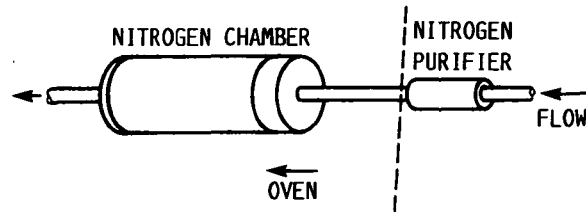


FIGURE 1. - SCHEMATIC OF NITROGEN AGING CHAMBER.

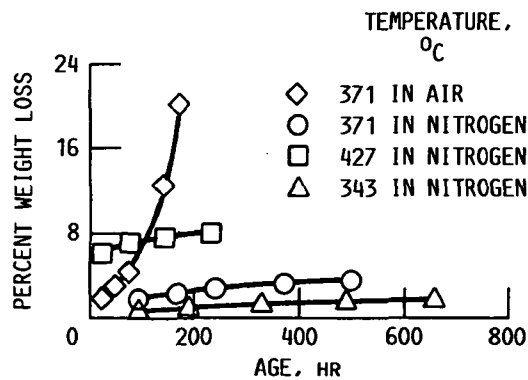


FIGURE 2. - NITROGEN AND AIR AGING OF UNIDIRECTIONAL CELION 6000/PMR-15 COMPOSITES.

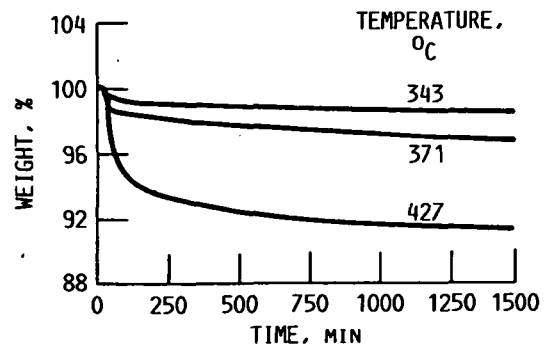


FIGURE 3. - TGA ISOTHERMAL WEIGHT LOSS OF CELION 6000/PMR-15 COMPOSITES IN ARGON.

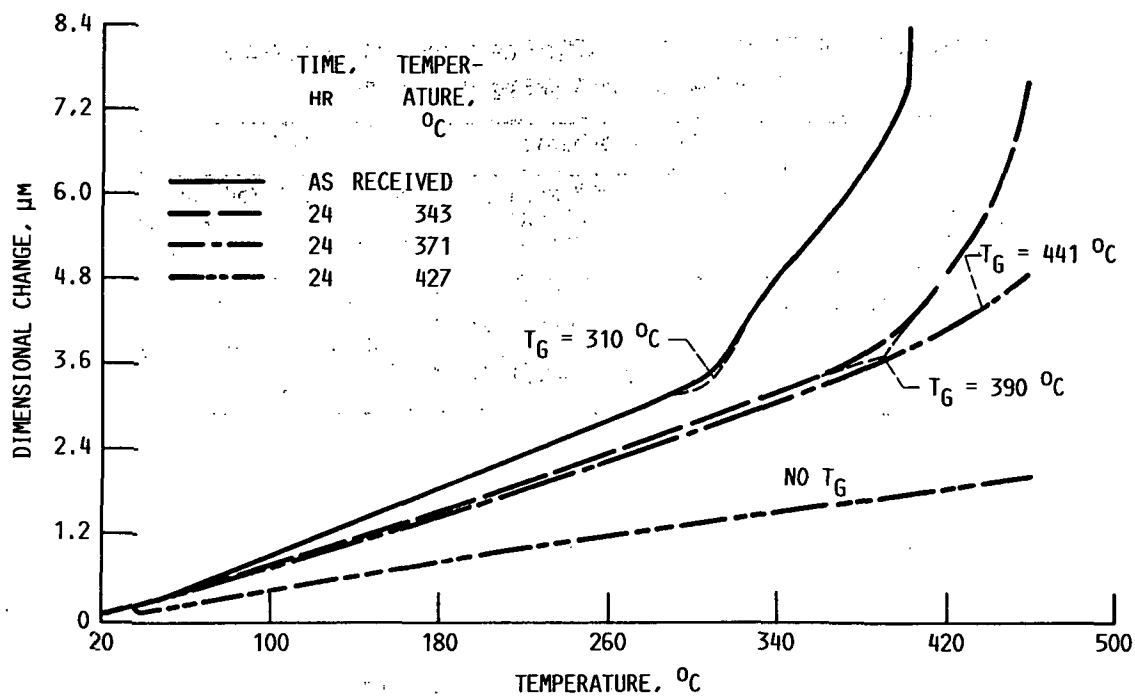


FIGURE 4. - TMA CURVES FOR CELION 6000/PMR-15 COMPOSITES.

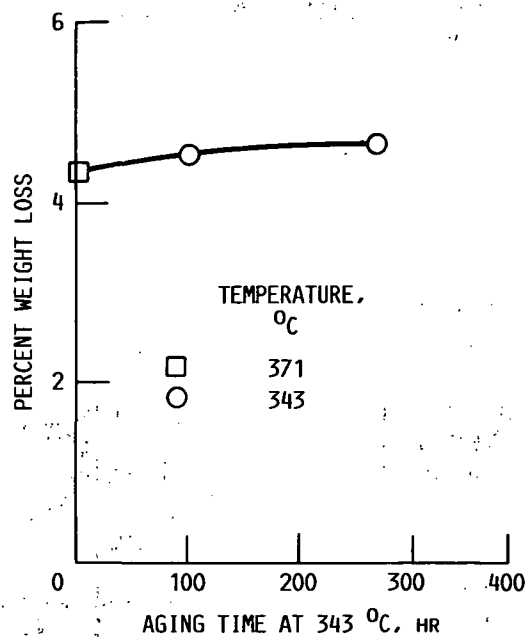


FIGURE 5. - THE EFFECTS OF NITROGEN AGING OF CELION 6000/PMR-15 COMPOSITE AT 371 °C ON THIS WEIGHT LOSS BEHAVIOR OF THE COMPOSITE AT 343 °C.

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